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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The continuation of a coordinated experimental and theoretical investigation of photoluminescence quenching and excited-state absorption, major loss mechanisms in potential tunable laser materials, is reported. The materials investigated include chromium-doped crystals of cubic elpasolite structure: $\text{Cs}_2\text{NaYCl}_6$, K_2NaScF_6 and K_2NaGaF_6 . Photoluminescence lifetimes, measured as functions of temperature and pressure in a diamond-anvil cell, revealed a pressure-induced shift of		

20. ABSTRACT (continued)

the onset of thermal quenching to higher temperatures. This observation is consistent with the predictions of a theoretical model, proposed earlier, in which radiationless de-activation of the chromium complex is mediated by quadratic coupling to an asymmetric vibrational mode. Ab-initio embedded-molecular-cluster calculations yielded predictions of the pressure dependence of local compressibility and localized vibration frequencies in good accord with experiment, thus demonstrating the predictive capability of theoretical modeling. Raman-scattering measurements in the diamond-anvil cell provided information about the pressure dependence of both localized and host-lattice vibration frequencies. Two-photon absorption experiments designed to characterize the vibronic structure of excited states are in progress, as a prelude to the investigation of excited-state absorption spectra.

RADIATIONLESS TRANSITIONS AND EXCITED-STATE ABSORPTION OF
LOW-FIELD CHROMIUM COMPLEXES IN SOLIDS

FINAL TECHNICAL REPORT

Ralph H. Bartram

July 20, 1989

U.S. Army Research Office

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FOREWORD

The theory of thermally activated radiationless transitions is well understood in principle, but there is a paucity of examples of its detailed quantitative application to well characterized systems, especially in the intermediate-coupling regime occupied by transition-metal complexes. An analogous situation prevails in the case of excited-state absorption. The aggressive extension of theory has been made urgently imperative by the exploitation of such systems in potential tunable-laser materials, where fluorescence quenching and excited-state absorption are major loss mechanisms. Low-crystal-field chromium complexes in ordered perovskites of cubic elpasolite structure are a paradigm for vibronic laser materials based on transition-metal doping of ionic crystals. The reported investigation has helped to identify those factors which control these important loss mechanisms. Computer modeling by embedded-molecular-cluster calculations may facilitate formulation of design criteria for such materials.

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STATEMENT OF PROBLEM STUDIED

Fluorescence quenching and excited-state absorption are major loss mechanisms in potential tunable-laser materials. The object of the reported investigation was to achieve a quantitative understanding of the factors which control such processes. The ultimate goal is to develop theoretical models with genuine predictive capability, in order to provide guidance in the selection of potential tunable-laser materials by permitting their a-priori evaluation with respect to these loss mechanisms. The subject of the present report on ARO Contract No. DAAL03-86-K-0017 is the extension and continuation of an investigation of thermal luminescence quenching in low-field chromium complexes in ordered perovskites with cubic elpasolite structure, which was initiated under ARO Contract No. DAAG29-82-K-0158 and will continue under ARO Contract No. DAAL03-89-K-0059. Experimental techniques employed in this investigation for characterizing low-field chromium complexes and for evaluating radiationless-transition rates include photoluminescence and Raman spectroscopy, at both ambient and high pressures, and two-photon excitation spectroscopy. Radiationless-transition rates are calculated by computer line-shape simulations, constrained by empirical spectral information, in order to identify the dominant photoluminescence-quenching mechanism. Ab-initio embedded-molecular-cluster calculations are employed in the development of theoretical models with predictive capability.

SUMMARY OF RESULTS

I. Introduction

Low crystal-field complexes of Cr^{3+} are characterized by broad-band (${}^4\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$) fluorescence, in contrast with high-field complexes which exhibit narrow-band (${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$) phosphorescence. This property, together with a large Stokes shift, make these low-field complexes ideal candidates for tunable solid-state vibronic laser applications. Examples of host crystals for chromium-based vibronic lasers include alexandrite¹, emerald² and gadolinium scandium gallium garnet (GSGG)³. However, the strong electron-lattice coupling which lends useful properties to these and analogous materials also enhances their susceptibility to both thermal quenching of fluorescence and excited-state absorption, related fundamental processes which proceed from the relaxed excited state of the laser-active center.

The project reported here involves a coordinated experimental and theoretical investigation of thermal fluorescence quenching and excited-state absorption in low-crystal-field chromium complexes in ordered perovskites of cubic elpasolite structure. This class of host materials possesses the virtue that a trivalent cation impurity can be accommodated in a rigorously octahedral site without charge compensation. Additionally, it provides chemical

sequences with a range of lattice parameters and crystal fields.

Under the previous contract, No. DAAG29-82-K-0158, fluorescence spectra and lifetimes were measured as functions of temperature in order to parameterize models and to determine activation energies and pre-exponential frequency factors for radiationless-transition rates.⁴ A theoretical model was proposed in which radiationless deactivation of the chromium complex is mediated by quadratic coupling to an asymmetric vibrational mode.⁵ Photoluminescence spectra measured in a diamond-anvil cell revealed a pressure-induced re-ordering of excited states with a consequent transition from low-field to high-field behavior, and a pressure-induced enhancement of localized vibration frequencies.⁶

Both experiments and computer modeling were extended during the period of the contract covered by this report, No. DAAL03-86-K-0017. Photoluminescence lifetimes, measured as functions of temperature and pressure in the diamond-anvil cell, revealed a pressure-induced shift of the onset of thermal quenching to higher temperatures.⁷ Ab-initio molecular-cluster calculations performed in conjunction with lattice-statics calculations (embedded-cluster calculations) yielded predictions of the pressure dependence of local compressibility and localized vibration frequencies in good accord with experiment. Raman-scattering measurements in the diamond-anvil cell provided

information about the pressure dependence of both localized and host-lattice vibration frequencies. Two-photon absorption experiments designed to characterize the vibronic structure of excited states are in progress. These developments are elaborated and assessed in the following sections.

II. Thermal-Quenching Mechanism in Chromium-Doped Elpasolites

Photoluminescence lifetimes of low-field chromium complexes, plotted as functions of temperature, display a characteristic, nearly discontinuous change in slope which signals the onset of thermal quenching.⁴ Analysis of lifetime data for the three host crystals studied in the present investigation, $\text{Cs}_2\text{NaYCl}_6$, K_2NaScF_6 and K_2NaGaF_6 , yielded thermal-quenching activation energies of 4250, 7270 and 9240 cm^{-1} , respectively, and pre-exponential frequency factors of order 10^{13} sec^{-1} . The measured temperature dependence of photoluminescence spectra served to characterize the chromium complex. The challenge was to account for the observed thermal-quenching behavior in terms of a theoretical model whose parameters were severely constrained by empirical spectral information.

There exists an extensive literature on the theory of radiationless transitions spanning fifty years. In the Mott theory,^{8,9} the activation energy for thermal fluorescence

quenching is identified with the difference between the crossing energy of the adiabatic potential energy surfaces and the minimum of the surface associated with the excited electronic state. Since the parameters of a single-configuration-coordinate, linear-coupling model are completely determined by the temperature dependence of the photoluminescence spectrum, the Mott theory can be readily tested. It fails by twenty orders of magnitude to explain the observed radiationless transition rate in the present application.

The modern, formal development of the theory of radiationless transitions proceeds from the pioneering contributions of Huang and Rhys¹⁰ and Lax¹¹. Since no radiationless transitions are possible between exact eigenstates of a physical system, the radiationless transition rate depends on the non-stationary state which is prepared in a given experiment.¹² In the adiabatic-coupling scheme, radiationless transitions are assumed to proceed from Born-Oppenheimer states and are mediated by the non-adiabaticity operator. First-order, time-dependent perturbation theory then leads to an expression for the radiationless transition rate W_{NR} of the form

$$W_{NR} = \nu\omega_p [\bar{n}G(\Omega_0 + \omega_p) + (\bar{n}+1)G(\Omega_0 - \omega_p)], \quad (1)$$

$$\bar{n} = [\exp(\hbar\omega_p/k_B T) - 1]^{-1}. \quad (2)$$

It is convenient to distinguish between promoting modes, which mix electronic states of different symmetries, and accepting modes, which absorb their energy difference.¹³ Coupling to accepting modes is reflected in the normalized line-shape function $G(\Omega)$, where Ω is measured from the zero-phonon line and $\hbar\Omega_0$ is the energy gap to be spanned in the multi-phonon transition. The promoting-mode interaction is incorporated in the factor $\nu\omega_p$, where ω_p is the promoting-mode angular frequency.

Several investigators have demonstrated the equivalence of adiabatic and static-coupling schemes at a certain level of approximation^{14, 15, 16, 17, 18}, and have discredited the popular "Condon approximation" introduced by Huang and Rhys¹⁰. The static-coupling scheme provides the most tractable formula¹⁸ for ν ,

$$\nu = (\pi/\hbar\omega_p^2) |\langle \phi(f;0) | \partial \mathcal{H} / \partial Q_p | \phi(i;0) \rangle|^2, \quad (3)$$

where Q_p is the promoting-mode configuration coordinate. A promoting mode of t_{1g} symmetry is required in order to couple the ${}^4T_{2g}$ excited state with the ${}^4A_{2g}$ ground state. Counter-rotating displacements of anion octahedra about trivalent and monovalent cations were found to provide a strongly coupled mode of the required symmetry¹⁹, contrary to earlier speculation concerning promoting-mode selection rules²⁰. The promoting-mode factor ν ,

calculated from Eq. (3) with free-ion chromium d orbitals and the exact nuclear potential for the ligands, is of the order of 10^{15} sec^{-1} for all three host crystals.⁵

The central problem in the application of radiationless-transition theory is evaluation of the normalized line-shape function $G(\Omega)$ in Eq. (1), which also describes the wavelength dependence of the fluorescence spectrum, for values of its argument which are very far from the range of arguments accessible to direct observation. Values of $G(\Omega_0 \pm \omega_p)$ are extremely sensitive to the precise physical model of the system which is adopted when the parameters of the model are constrained by empirical spectral information. Models based on linear coupling to modes of a_{1g} symmetry were found to fail by six to eight orders of magnitude to explain the observed radiationless-transition rate, even when a range of vibration frequencies was considered.⁵

The failure of linear-coupling models suggested consideration of quadratic coupling; i.e., different vibration frequencies in the two electronic states. Although quadratic coupling to a_{1g} modes is possible in principle, it is ruled out in the present system by direct experimental evidence. The octahedral chromium complex has additional degrees of freedom, however, and coupling to lower symmetry accepting modes is permitted by the orbital degeneracy of the ${}^4T_{2g}$ excited state. A simplified model was considered⁵ which

includes just two electronic states, the ${}^4A_{2g}$ ground state and one orbital component of the ${}^4T_{2g}$ excited state, with linear coupling to a single a_{1g} accepting mode and quadratic coupling to a single t_{2g} accepting mode. The single a_{1g} accepting mode in this model is an effective mode representing both a_{1g} and e_g modes, which actually have comparable linear coupling²¹. Normalized line-shape functions were calculated for each mode by the method of Struck and Fonger²², in which individual vibrational overlap integrals are evaluated by a recursion formula, and the composite line shape was calculated by numerical convolution. Both the a_{1g} and ground-state t_{2g} vibration frequencies were treated as adjustable parameters, but the strength of quadratic coupling was calculated ab-initio from a point-ion model. Not only was it possible to fit the temperature dependence of fluorescence spectra and the activation energy for thermal quenching simultaneously, but the model also yielded the correct order of magnitude for the absolute radiationless-transition rate when the estimated value of the promoting-mode factor was used. Furthermore, the model worked equally well for all three elpasolite compounds considered, and the adjusted ground-state t_{2g} vibration frequencies are in good agreement with independently determined values.

III. Pressure Dependence of Chromium Photoluminescence

Photoluminescence experiments under intense hydrostatic pressure were undertaken in order to provide systematic control of the physical parameters as an aid in the development and testing of physical models. Photoluminescence spectra and lifetimes of $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$ and $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$ were measured with chopped He-Cd laser excitation at pressures between 0 and 6.5 GPa (65 kbars) and at controlled temperatures between 150 and 300 K, by means of a diamond-anvil high-pressure cell mounted in a cold-finger dewar. In both compounds a transition from low-field to high-field behavior, reflecting a crossing of the $^4\text{T}_{2g}$ and $^2\text{E}_g$ energy levels, is evidenced by a pronounced blue shift of the featureless fluorescence spectrum and its ultimate replacement by a highly structured phosphorescence spectrum.⁶ This transition is further attested by an order-of-magnitude increase in radiative lifetime at high pressure. The measured luminescence lifetimes reflect only the change from fluorescence to phosphorescence; thermal quenching in fluoride elpasolites was neither expected nor observed in the accessible temperature range. Finally, from its temperature dependence it is evident that a residual broad fluorescence spectrum at high pressure originates in a thermally populated state; although it is prominent at room temperature, it is no longer in evidence at 150 K.

The vibronic structure of the high-pressure, low-temperature phosphorescence spectrum of $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$, which is susceptible to interpretation by analogy with the resolved low-temperature spectrum of the high-field compound $\text{K}_2\text{NaAlF}_6:\text{Cr}^{3+}$,²³ provides quantitative information about the vibration frequencies and electron-lattice coupling at high pressure. The vibration frequencies at $P = 6.1$ GPa and $T = 154$ K were compared with published values at ambient pressure and $T = 4$ K.^{23,24} Increases of about 12 % were evident; i.e. 2 % per GPa.

A similar phosphorescence spectrum with well resolved vibronic structure is observed for $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$ at high pressure and low temperature, with the difference that the zero-phonon line and each of its replicas is split. This splitting is evidence of a phase transition, occurring just below room temperature, which removes the degeneracy of the ${}^2\text{E}_g$ excited state. The ambient-pressure photoluminescence spectrum was also measured at liquid-helium temperature for comparison, and the vibration frequencies were again found to increase at the rate of 2 % per GPa.

Photoluminescence spectra of $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$ were measured with Ar-ion-laser excitation at pressures between 0 and 11.5 GPa and at controlled temperatures between 80 and 300 K. This compound

exhibits an even more pronounced blue shift than the fluoride elpasolites, but no evidence of level crossing is observed; the low-temperature spectrum at the highest pressure resembles that at ambient pressure²¹, and is characteristic of ${}^4T_{2g} \rightarrow {}^4A_{2g}$ emission. Resolved vibronic structure at high pressure and low temperature is currently being analyzed.

The observed low-field to high-field transition in the fluoride compounds and blue shift of the broad band in all three compounds are attributed primarily to a substantial pressure-induced enhancement of the crystal-field parameter Dq , associated with reduction of the lattice parameter. The pronounced non-linear pressure dependence of Dq suggests a local-strain effect, as well. Spectral data on all three compounds were analyzed to extract a pressure-dependent local compressibility $K(P)$, defined by

$$K(P) = -(3/r_0')dr_0'/dP, \quad (4)$$

where r_0' is the equilibrium chromium-ligand distance in the relaxed ${}^4T_{2g}$ excited state. This local compressibility is plotted as a function of pressure for $K_2NaScF_6:Cr^{3+}$ in Fig. 1. The increase in vibration frequencies with pressure is a manifestation of the anharmonicity of pair potentials. The measured rate of increase yields a local Grüneisen parameter for each mode.

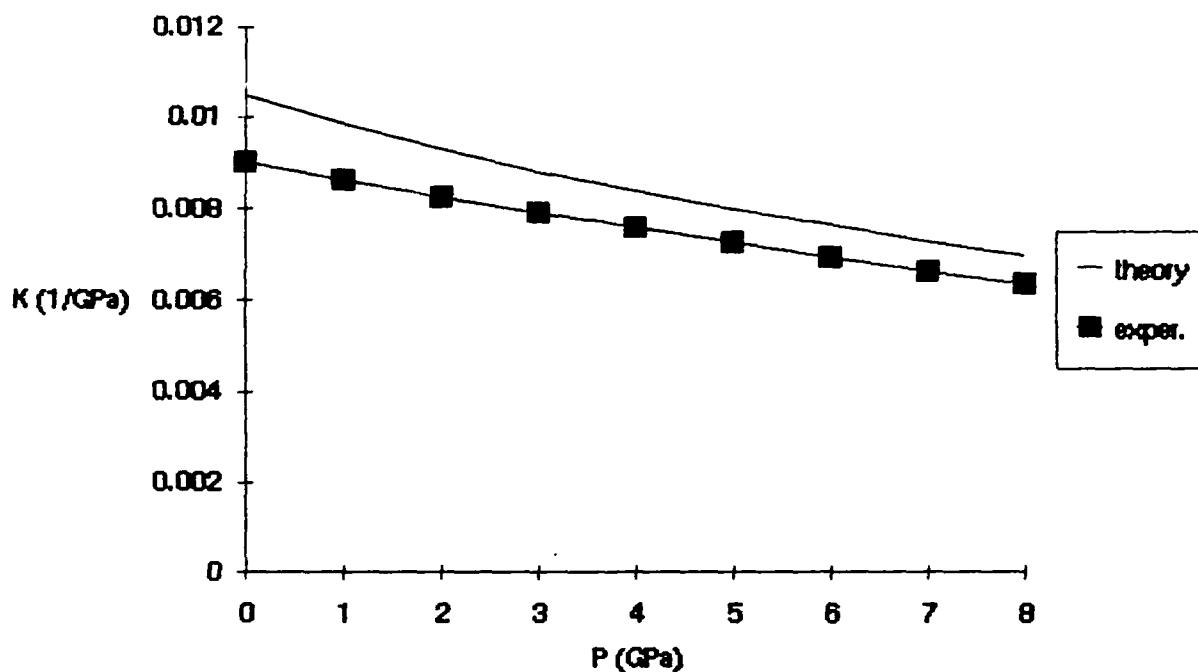


Figure 1. Local compressibility as a function of pressure for $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$. The experimental values are inferred from the measured blue shift of the broad luminescence band. The theoretical curve is derived from *ab-initio* calculations on an embedded-molecular-cluster model.

Thermal quenching of fluorescence in the chloride elpasolite, $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$, does occur in the temperature range accessible to our high-pressure apparatus. This material then provides an opportunity to investigate the dependence of activation energy for thermal quenching on the crystal-field parameter Dq and the vibration frequencies in a single host crystal for comparison with theoretical predictions.

The chloride compound exhibits thermal quenching in the temperature range 250 K - 350 K at ambient pressure,⁴ with activation energy 4250 cm^{-1} . In order to test the predictions of our model, we measured the luminescence lifetime as a function of temperature at elevated pressures;⁷ preliminary data are plotted in Fig. 2. These measurements were made with pulsed Nd:YAG laser excitation in the diamond-anvil cell mounted on the cold-finger dewar. The onset of thermal quenching was found to be shifted to higher temperature by 40 K at a nominal pressure of 0.2 GPa (2 kbars), corresponding to an apparent increase in activation energy at the rate of $3000\text{ cm}^{-1}/\text{GPa}$. The diamond-anvil cell employed in these measurements was fabricated partly at GTE Laboratories, Inc. in Waltham, MA, and partly at the University of Connecticut, based on an NBS design²⁵. It incorporated an accidental and somewhat unfortunate design feature, an epoxy resin used to mount the diamonds, which limited its use to temperatures less than 350 K. A new diamond-anvil cell constructed at the University of

Connecticut employs an alternative system for mounting the diamonds and incorporates a heating coil which permits considerably higher temperature operation. Photoluminescence lifetime measurements were recently extended to higher temperatures (550 K) and pressures (3 GPa), using the newly constructed diamond-anvil cell, and it now appears that the rate of increase is less than $1500 \text{ cm}^{-1}/\text{GPa}$. The discrepancy is attributed to the uncertainty in measuring small changes in pressure in a diamond-anvil cell.

Calculations based on the two-accepting-mode, linear- and quadratic-coupling model were performed in order to simulate the effects of pressure on thermal luminescence quenching in $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$.⁷ Values of the energy gap $\hbar\Omega_0$ and the a_{1g} and ground-state t_{2g} vibration frequencies were systematically adjusted and temperature-dependent radiationless transition rates W_{NR} were calculated from the corresponding line-shape simulations for fixed S_0 , using Eq. (1) with a fixed value of ν . A pressure-induced increase in the quenching temperature is predicted, as shown in Fig. 3. The pressure dependence of the energy gap can be inferred from blue-shift measurements, but it remains to determine the pressure dependence of the localized vibration frequencies in this material in order to make a precise quantitative prediction. The observed pressure dependence of thermal quenching is qualitatively as expected from the model.

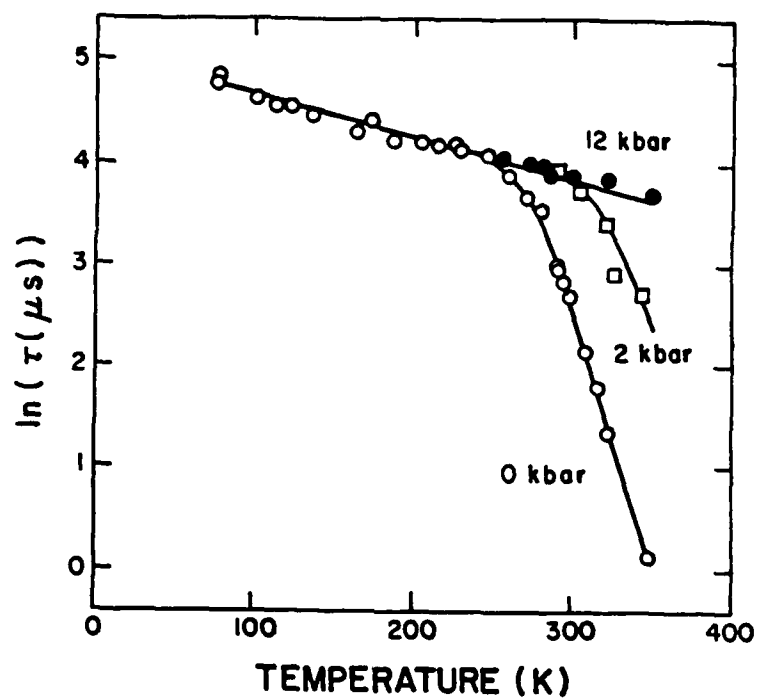


Figure 2. Measured temperature and pressure dependence of luminescence lifetimes for $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$.

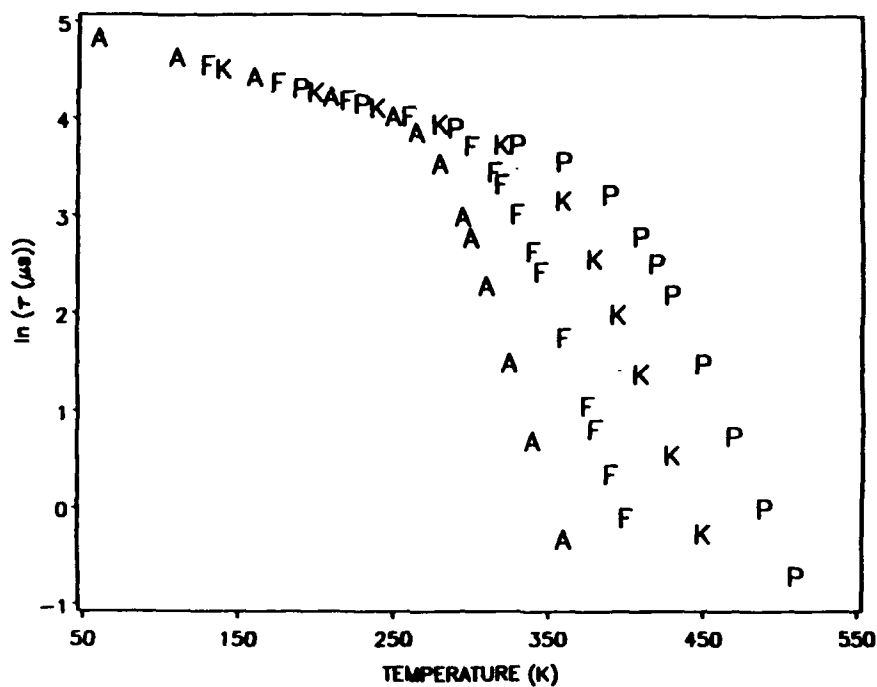


Figure 3. Predicted temperature and pressure dependence of luminescence lifetimes for $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$. Curve A is adjusted to fit experiment at ambient pressure. Curves F, K and P correspond, respectively, to 5%, 10% and 15% increases in the energy gap and vibration frequencies.

High-pressure photoluminescence measurements on chromium complexes in elpasolites have proved to be particularly revealing of their properties and processes. Both the pressure-induced re-ordering of energy levels and the pressure dependence of thermal quenching are dramatic results which challenge theoretical interpretation.

IV. Computer Modeling of Low-Field Chromium Complexes

Ab-initio molecular-cluster calculations were performed in both the $^4A_{2g}$ ground state and the $^4T_{2g}$ excited state of the chromium complex in all three host crystals. These calculations were performed with an SCF-MO program called MELD.²⁶ The 1s, 2s and 2p shells of chromium and the nearest-neighbor chlorine ions were replaced by effective-core potentials, while the valence orbitals were explicitly included. All nearest-neighbor fluorine orbitals were included, but the nearest sodium and potassium ions were represented by bare effective core potentials.

Lattice-statics calculations were performed on all three host crystals, using the HADES III program acquired from AERE, Harwell²⁷, in order to determine the pressure P as a function of lattice parameter. We have recently effected a modification, called HADESR, of the lattice-statics program HADES III, which permits it to be interfaced directly with a molecular-cluster calculation by removing its restriction to pair potentials in the

region occupied by the cluster. An adiabatic potential energy function for the cluster is obtained by calculating its total energy as a function of geometry using the MELD program (or any other suitable method). This function is fit to a polynomial in symmetry-adapted coordinates and is used to update energies and forces in each iteration of the lattice-statics calculation. In effect, the cluster is extended by incorporating pair-potential interactions with the rest of the lattice, and the geometry search is performed automatically.

The equilibrium geometry of the cluster in its ${}^4A_{2g}$ ground state was calculated as a function of lattice parameter by the HADESR method for all three compounds. Vibration frequencies of modes of a_{1g} , e_g and t_{2g} symmetry, about the equilibrium configuration, were also calculated as functions of lattice parameter. These results were combined with the HADES III calculations of pressure as a function of lattice parameter to yield vibration frequencies as a function of pressure. The calculated frequencies in the fluoride compounds were compared with values inferred from resolved vibronic structure of photoluminescence spectra⁶. Theoretical values were found to be too high by about 15 %; this systematic discrepancy is attributed to the neglect of electron correlation effects. The predicted pressure dependence agrees well with experiment.

Similar calculations are in progress for the ${}^4T_{2g}$ excited state. The HADESR method is employed to determine the equilibrium geometry with respect to fully symmetrical displacements only; the symmetrical configuration is then used as a starting point for the exploration of lower symmetry, Jahn-Teller distortions involving just anion displacements. Vibration frequencies are calculated in the excited state as well. These calculations, in conjunction with those for the ground state, will provide predictions of absorption and emission energies, Huang-Rhys factors and Jahn-Teller coupling constants, and the degree of quadratic coupling. These parameters control the radiationless-transition rate and govern excited-state absorption; their precise determination is therefore a major goal of the present investigation.

The chromium-ligand distance in the excited state, r_0' , calculated as a function of pressure, permits a theoretical prediction of the local compressibility $K(P)$ defined by Eq. (4). Calculated values for $K_2NaScF_6:Cr^{3+}$ are compared with experiment in Fig. 1, with good agreement.

V. Raman Spectroscopy

Raman scattering experiments were performed with argon-ion-laser excitation, photon counting and signal averaging. Measurements

were made on a number of halide elpasolites at both ambient pressure and high pressures, the latter in the diamond-anvil cell. Polarized Raman scattering measurements on an oriented single crystal of $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$, supplied by Dr. David Gabbe of MIT, provided unambiguous identification of the four Raman-active vibrational modes of the host lattice. In descending order of vibrational frequency, they are a_{1g} , e_g and t_{2g} modes of the ScF_6^{3-} octahedron, and a t_{2g} mode of the ScK_8^{11+} cube. Measurements at reduced temperatures revealed two additional effects: Splitting of the lower frequency t_{2g} Raman line provides evidence of a phase transition, detected earlier in high-pressure photoluminescence spectra and verified recently by low-temperature ESR spectroscopy; and side-band structure of the a_{1g} Raman line, attributed to localized modes of the chromium impurity on the basis of its concentration dependence, is displayed with enhanced resolution. Unpolarized Raman spectra of $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$, $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$ and $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$ were measured as functions of pressure in the diamond-anvil cell. These data yield the pressure dependence of host-lattice modes and, in the case of the scandium compound with 5 % chromium concentration, of the a_{1g} and t_{2g} localized modes. The local-mode frequencies inferred from Raman and photoluminescence spectra are in agreement. They are not precisely the same as those of the host-lattice modes, nor do they increase with pressure at precisely the same rate.

VI. Two-Photon Excitation Spectroscopy

Two-photon excitation spectroscopy at low temperature has been employed by McClure and co-workers in related investigations.²⁸ This technique has the virtue that two-photon transitions between electronic states of the same parity are electric-dipole allowed, whereas one-photon transitions are forbidden. Consequently, the vibronic structure of the spectrum is greatly simplified, since progressions of even-mode phonon replicas are built on a prominent zero-phonon line rather than on false origins associated with odd modes. The object of the present investigation is to characterize the vibronic states of a single crystal of $\text{K}_2\text{NaScF}_6:\text{Cr}^{3+}$ in detail in order to refine the model for thermal quenching of photoluminescence and to establish the predictability of excited-state absorption spectra. Preliminary two-photon spectra of the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ transition have been obtained with Raman-shifted, Nd:YAG-pumped dye-laser excitation at liquid-helium temperature. The zero-phonon line has been observed, together with several phonon replicas. The two-photon spectrum of the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transition, which occurs at longer wavelength, will also be investigated. These data will be used to parameterize models for the vibronic structure of the relevant electronic states. Ultimately, the spectrum of the ${}^4\text{T}_{2g} \rightarrow {}^4\text{T}_{1g}$ transition will be measured in excited-state absorption and compared with predictions based on two-photon excitation spectra.

PUBLICATIONS

Publications generated under ARO Contracts DAAG29-82-K-0158 and DAAL03-86-K-0017, including refereed journal articles and proceedings, theses and presentations at meetings are listed below. Those attributable to the earlier contract are distinguished by an asterisk, and are included here for completeness, since most of them appeared in print during the period of the later contract.

A. Journal Articles and Proceedings

- *1. R.H. Bartram, "Theory of fluorescence quenching in low-field chromium complexes in solids", in *Tunable Solid State Lasers*, Eds. P. Hammerling, A.B. Budgor and A. Pinto (Springer-Verlag, Berlin and Heidelberg, 1985) pp. 155-163
- *2. R.H. Bartram and A.M. Stoneham, "Alternative forms for the promoting interaction in radiationless transitions", *J. Phys. C: Solid State Phys.* 18, L549-L553 (1985)
- *3. J.F. Dolan, L.A. Kappers and R.H. Bartram, "Pressure and temperature dependence of chromium photoluminescence in $K_2NaGaF_6:Cr^{3+}$ ", *Phys. Rev. B* 33, 7339-7341 (1986)
- *4. L.J. Andrews, B.C. McCollum and R.H. Bartram, " Cr^{3+} in K_2NaScF_6 : crystal growth and spectroscopy", *Proceedings of the First International Laser Science Conference, Dallas, Texas, 1985*, pp. 225-228

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1. James F. Dolan, Pressure and temperature dependence of chromium photoluminescence in solids, Doctoral dissertation, University of Connecticut, 1988
2. John C. Charpie, Thermal quenching of chromium fluorescence in solids, Doctoral dissertation, University of Connecticut, 1988

C. Presentations at Meetings

- *1 R.H. Bartram, J.C. Charpie, L.J. Andrews and B.C. McCollum, "Mechanism of fluorescence quenching in low-field chromium complexes", Bull. Am. Phys. Soc. 29, 538 (1984)
- *2 R.H. Bartram, "Theory of fluorescence quenching in low-field chromium complexes in solids", First Annual Conference on Tunable Solid State Lasers, LaJolla, California, June 13-15 (1984) (invited paper)
- *3 R.H. Bartram, J.C. Charpie, J.F. Dolan, L.J. Andrews and B.C. McCollum, "Mechanism of fluorescence quenching in low-field chromium complexes", International Conference on Defects in Insulating Crystals, Salt Lake City, Utah, August 20-24 (1984)
- *4 J.F. Dolan, L.A. Kappers and R.H. Bartram, "Pressure dependence of chromium photoluminescence in ordered perovskites", Bull. Am. Phys. Soc. 30, 420 (1985)
- *5 J.F. Dolan, L.A. Kappers and R.H. Bartram, "Pressure and temperature dependence of chromium photoluminescence in ordered perovskites", Bull. Am. Phys. Soc. 30, 1135-1136 (1985)

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- *7. L.J. Andrews, B.C. McCollum and R.H. Bartram, " Cr^{3+} in K_2NaScF_6 : crystal growth and spectroscopy", First International Laser Science Conference, Dallas, Texas, November 18-22 (1985)
8. R.H. Bartram, J.F. Dolan, J.C. Charpie, A.G. Rinzler and L.A. Kappers, "Pressure dependence and thermal quenching of chromium photoluminescence in ordered perovskites", Fifth Europhysics Topical Conference on Defects in Ionic Crystals, El Escorial, Spain, September 8-12 (1986)
9. R.H. Bartram, A.G. Rinzler, J.C. Charpie and L.A. Kappers, "Pressure dependence of fluorescence quenching in a chromium-doped ordered perovskite", Bull. Am. Phys. Soc. 32, 821 (1987)
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